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Abstract	<p>Water and surface sediment samples from Rivers Sabaki, Ramisi and Vevesi that flow into the Indian Ocean coast of Kenya were analysed for heavy metals. The sediment concentrations of exchangeable cations (in $\mu\text{g/g}$) for Co, Cu, Mn, Ni, Pb, Sn and Zn ranged from 0.10 to 506.75 (for Mn at Sabaki), constituting between 2% and 20% of the total metal concentrations obtained by digestion with strong acid. Cu, Mn, Ni, Pb and Zn were more leachable with 0.1 N HCl. The total dissolved metal in water and the total sediment concentrations for Ag, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn and Zn are given in the text. For dissolved metals, the metal/Mn ratios indicated higher concentrations of Ag in Sabaki River, Cd in Ramisi, Ni in Sabaki and Pb in Ramisi, respectively. In sediments, the metal/Mn ratios showed higher enrichment of Ag in Ramisi, Cd in Sabaki and Vevesi, and Zn in Sabaki, respectively. Enrichment factors showed elevated levels of Cd, Pb and Zn in sediment in River Sabaki and River Vevesi that were due to anthropogenic inputs through Athi River. The total dissolved metal concentration ranges for the three rivers were comparable with those ranges reported in</p>	

rivers in South Africa but the sediment concentrations were below those of rivers in Europe and Asia where anthropogenic addition of some of the toxic elements such as Cu, Pb and Cd is evidently higher.

Keywords (separated by '-') Water, surface sediment - Heavy metals - Rivers - Indian Ocean Coast of Kenya - Enrichment factors

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1

2 Anthropogenic Sources of Heavy Metals in the Indian Ocean 3 Coast of Kenya

4 E. Z. Ochieng · J. O. Lalah · S. O. Wandiga

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7 **Abstract** Water and surface sediment samples from
8 Rivers Sabaki, Ramisi and Vevesi that flow into the Indian
9 Ocean coast of Kenya were analysed for heavy metals. The
10 sediment concentrations of exchangeable cations (in $\mu\text{g/g}$)
11 for Co, Cu, Mn, Ni, Pb, Sn and Zn ranged from 0.10 to
12 506.75 (for Mn at Sabaki), constituting between 2% and
13 20% of the total metal concentrations obtained by digestion
14 with strong acid. Cu, Mn, Ni, Pb and Zn were more
15 leachable with 0.1 N HCl. The total dissolved metal in
16 water and the total sediment concentrations for Ag, Cd, Co,
17 Cr, Cu, Mn, Ni, Pb, Sn and Zn are given in the text. For
18 dissolved metals, the metal/Mn ratios indicated higher
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20 Sabaki and Pb in Ramisi, respectively. In sediments, the
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22 Ramisi, Cd in Sabaki and Vevesi, and Zn in Sabaki,
23 respectively. Enrichment factors showed elevated levels of
24 Cd, Pb and Zn in sediment in River Sabaki and River
25 Vevesi that were due to anthropogenic inputs through Athi
26 River. The total dissolved metal concentration ranges for
27 the three rivers were comparable with those ranges reported
28 in rivers in South Africa but the sediment concentrations
29 were below those of rivers in Europe and Asia where
30 anthropogenic addition of some of the toxic elements such
31 as Cu, Pb and Cd is evidently higher.
32

Keywords Water, surface sediment · Heavy metals · 33
Rivers · Indian Ocean Coast of Kenya · Enrichment factors 34

35 Studies on heavy metal pollution of river systems have 35
36 recently attracted a lot of attention due to the need for 36
37 acceptable drinking water quality and better understanding 37
38 of environmental pollution of freshwater resources (Lee 38
39 et al. 1998; Neal et al. 2000; Huang and Lin 2003; Powell 39
40 and Alexander 2003; Reimann et al. 2003; Jain 2004; 40
41 Adamo et al. 2005; Nyangababo et al. 2005; Okonkwo 41
42 et al. 2005; Demirak et al. 2006; Deheyn and Latz 2006; 42
43 Grosbois et al. 2006; Nicolau et al. 2006). Inland rivers and 43
44 streams are also important sources of anthropogenic metal 44
45 deposits into the seas and oceans (Everaarts and Nie- 45
46 uwenhuize 1995; Milward and Lin 2003; Adamo et al. 46
47 2005; Nicolau et al. 2006). Unlike organic contaminants, 47
48 natural processes of decomposition do not remove heavy 48
49 metals; instead heavy metals can be enriched by aquatic 49
50 organisms and can therefore be converted to organic 50
51 complexes that may even be more toxic (Jain 2004). 51
52 Although fractionation is useful in determining the bio- 52
53 availability and toxicity of heavy metals, the total content 53
54 of heavy metals in water and sediment is useful in mapping 54
55 out various hot spots as well as for identification of 55
56 anthropogenic inputs (Lee et al. 1998; Huang and Lin 56
57 2003). Apart from human and industrial effluents, weath- 57
58 ering of soil and rocks and volcanic eruptions are also other 58
59 main sources of heavy metals discharging into the marine 59
60 environment. 60

61 Since metal solubility is principally controlled by 61
62 environmental pH, its concentration, its various types of 62
63 species and oxidation states, the organic ligands and the 63
64 redox environment of the aquatic system (Lee et al. 1998; 64
65 Huang and Lin 2003; Davis and Leckie 1978; Jeon et al. 65

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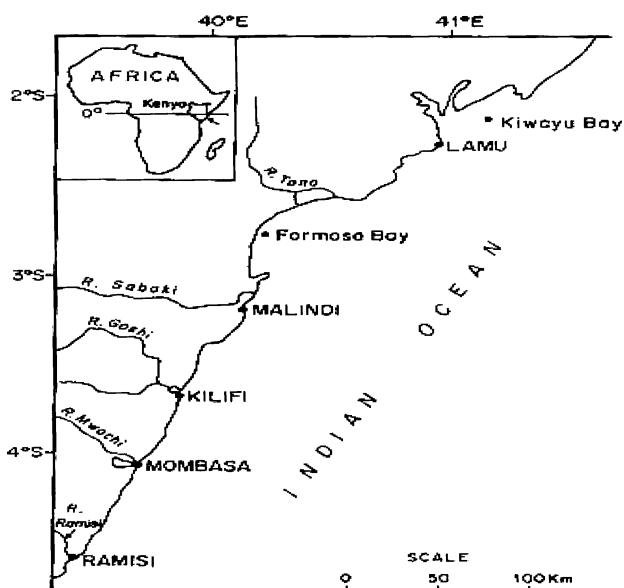


Fig. 1 The Indian Ocean coastal area showing R. Sabaki and R. Ramisi where samples were taken

2003; Milward and Lin 2003; Warren et al. 2005; Grosbois et al. 2006), we expect heavy metal speciation in riverine systems to be unique and the total content to contribute significantly to the concentrations in the oceans or seas where the rivers discharge into (Berg et al. 1995; Cheevaporn et al. 1995; Everaarts and Nieuwenhuize 1995; Deheyn and Latz 2006; Nicolau et al. 2006). The determination of the physico-chemical parameters of natural waters such as pH, temperature, dissolved oxygen demand (DOD), turbidity, and alkalinity is also pertinent because they can modify heavy metal chemistry and toxicity on aquatic life and consequently act as indicators of water pollution (Everaarts and Nieuwenhuize 1995; Lim et al. 1995; Demirak et al. 2006; Deheyn and Latz 2006). Although, developing countries have been considered least polluted in the past, rapid industrial development and high population growth rates in these decades have gradually degraded quality of some of their natural waters and, subsequently, the coastal waters as the final recipients (Cheevaporn et al. 1995; Lee et al. 1998; Huang and Lin 2003). This paper reports on bioavailable heavy metal concentrations, total heavy metal content, and metal enrichment in surface estuarine sediment and water samples in three rivers, River Sabaki, River Ramisi and River Vevesi, as they discharge into the Indian Ocean Coast of Kenya (Fig. 1).

Materials and Methods

The sampling sites were: at the shores/river mouths (Sabaki and Ramisi) into the Indian Ocean at the Indian Ocean

Coast in Kenya. The river sediments were mixtures of sand, silt and mud with varying proportions and degrees of compaction and characteristics and the samples were analysed for these physico-chemical characteristics. Generally the river mouths inside the entrance to the Ocean had coarse bottom sediments with considerable amounts of mud. Water and surface sediment samples were taken at about 1 km downstream from Ramisi Sugar Factory at Ramisi bridge (sample RMS2), at Daragube water pump (sample RMS1) upstream before the factory, in River Vevesi (a tributary of River Ramisi) at a point downstream from Daragube water pump (VVS) and from Sabaki River near the shore before getting into the Ocean (sample SB). Sampling sites were located at 4°36' S and 39°36' E (Ramisi samples) and at 3°10' S and 40°6' E (Sabaki bridge). Athi River flows from Ngong hills in central Kenya mainly through sand and rocks and mining industries for cement and other inorganic products at Athi River, through Yatta plateau, through major industries including tannery and food processing factories in Thika, through Ruiru and Limuru areas where agrochemicals and fertilizers are used in large scale coffee and tea farms and through municipal and domestic waste before joining into River Sabaki which discharges in to the Indian Ocean. River Ramisi flows through Shimba Hills in to the Indian Ocean at Ramisi and River Vevesi is a tributary of River Ramisi which has acidic pH because it passes through a bog downstream from Ramisi where sampling was done.

A sample of 500 mL of water was taken by immersing the bottles and lifting up and was mixed with 2 mL of concentrated HNO₃ to lower the pH of the water to <pH 2, filtered through 0.45 μm Millipore filters and stored in the fridge in the laboratory at 4°C before analysis. At each site additional samples of water were taken for analysis of electrical conductivity, pH, salinity and transparency. The temperature of the water was also determined in situ during sampling. Surface sediment (~0–2 cm layer) samples were taken from the same sites in triplicates using stainless steel Ekman grab, stored in polythene bottles and transported to the laboratory for storage at 4°C while awaiting analysis. The samples were taken during the rainy season in March. Before analysis, portions of sediment were mixed well and then a 20-g amount taken into a glass dish and dried at 105°C for 24 h in a Gallen Kamp oven, ground well in a Pestle and Mortar and sieved through 63 μm mesh sieve. The moisture content was determined by heating an aliquot at 105°C in the oven to obtain weight loss. The percent organic carbon content (OC) was also determined by heating in a furnace above 400°C. The rest of the sample was used for analysis of heavy metal.

A Perkin Elmer Atomic Absorption Spectrophotometer Model 2380 with an air/acetylene flame was used for analysis of the water and sediment samples after digestion

148 with concentrated HNO₃/HCl acid and preparation of
 149 appropriate calibration standards using the method of
 150 Ochieng (1987). The accuracy of the method for sediment
 151 analysis was tested using a fortified IAEA reference soil
 152 sample according to the IAEA established method which
 153 involved taking 2.5 g of soil, subdividing into 0.5 g sub-
 154 samples, followed by digestion with the acid and a high
 155 mean recovery of 91% was obtained for this fortified
 156 sample.

157 Results and Discussions

158 The OC was generally below 1% in all the estuarine sed-
 159 iment samples except for the silty-clay sediment at Sabaki
 160 site probably due to the greater primary productivity of the
 161 river mouth and high sediment load as a result of intense
 162 agricultural activities of Central Kenya highlands. River
 163 Sabaki is also known to experience a lot of siltation
 164 problems as well. Some of the sediment characteristics
 165 obtained were River Sabaki: pH 7.6, sand content (0.32%),
 166 silt content (42.5%), clay content (30.2%), Organic carbon
 167 (OC) content (4.7%), moisture content (MC; 20.3%), tex-
 168 ture (silty clay), and River Ramisi: pH 7.4, sand content
 169 (45.2%), silt content (14.3%), clay content (6.8%), OC
 170 (0.73%), MC (19.7%), texture (sandy loam). The shores
 171 and river mouths attested to the complex sedimentation
 172 processes derived through hydrologic erosion, transport
 173 and deposition as described for other aquatic environments.

174 At River Sabaki sampling site, the organic carbon could
 175 accumulate as a result of precipitation. These three coastal
 176 rivers flow through relatively dry areas with low annual
 177 rainfall. However, they provide sources of drinking water
 178 and irrigation. Anthropogenic and geological disturbances
 179 such as torrents of tropical rainfall, floods, soil erosion,
 180 siltation and industrial effluents are expected to influence
 181 the organic and inorganic loads which would register sig-
 182 nificant footprints in the estuarine sediments. Increase in
 183 sediment moisture content can induce reduced conditions,
 184 for example Cr³⁺ formation can be favoured by reduction
 185 of Cr⁴⁺ as a result of enhanced solubility and lability of

organic matter and at higher pH, higher concentration of
 Cd in sediment is found due to precipitation of dissolved
 Cd. The coastal rivers had four-times the dissolved salt
 content compared with other inland rivers which discharge
 into Lake Victoria (Ochieng 1987). They also had higher
 electrical conductivities of 320–382 μS/cm, higher tem-
 peratures as well as higher dissolved oxygen (DO) content.

The limnological data obtained for the sampling sites
 are shown in Table 1. From these data, the river water
 chemistry qualifies these rivers as suitable for aquatic life
 and for human use. The rivers Sabaki and Ramisi are
 slightly alkaline with mean pH values of 7.66 and
 7.22–7.50, respectively, with DO contents of 8.0 and
 5.7–7.0 mg/L (i.e. 95% and 72% saturation range),
 respectively, and low alkalinities in the sampling sites
 covered during the study. The temperatures (mean of
 26.4 ± 1.60°C) were within maximum productivity range.
 River Vevesi (a tributary of River Ramisi) is different as it
 passes through a bog going downstream before the sam-
 pling site. Its water was acidic and had much lower alka-
 linity, lower DO and slightly higher electrical conductivity
 which are common for such water. The content of dis-
 solved salts in freshwaters, as indicated by the electrical
 conductivity, has been used by some researchers as a
 general indication of their potential fertility. The electrical
 conductivities in freshwaters in Kenya, as has been found
 in the lakes, are influenced mainly by carbonate salts,
 which account for up to 80% of the conductivity in most
 cases. The remaining electrolytes are therefore present in
 low concentrations. Consequently the concentration of
 biologically valuable electrolytes such as phosphates and
 nitrates is therefore much lower in Kenyan freshwaters
 than expected (Ochieng et al. 2006; Ochieng et al. 2007).
 The water conductivity would be largely determined by
 Ca²⁺ and bicarbonate fluxes and would relate to these ions
 as does its pH. Table 2 shows the comparison of turbidity
 and DO content of the three rivers with those of interna-
 tional standards, considering different purposes for which
 their water is intended. According to these standards, these
 Kenyan rivers are not polluted and they fulfil the require-
 ments except for the turbidity of R. Sabaki which was very

Table 1 Some of the limnological data obtained for the coastal rivers studied

River	pH	Temp (°C)	DO (mg/L)	Transp (cm)	Turb (FTU)	Alkalinity mgCaCO ₃ /L	Cond μS/cm
SB	7.66	25.2	8.0 (95%)	80	220	85.0	320
RMS1	7.22	28.7	5.7 (72%)	25	22.0	63.03	335
RMS2	7.50	27.3	7.0 (88%)	25	16.0	60.61	350
VVS	6.33	26.4	4.6 (58%)	75	3.5	19.8	382

SB Sabaki River, RMS1 Ramisi site 1, RMS2 Ramisi site 2, VVS Vevesi, DO dissolved oxygen, Transp transparency, Turb turbidity, Cond electrical conductivity

Table 2 Comparing some of the limnological data of the rivers with international standard requirements for aquatic life in freshwaters

Purpose of utilization	pH	Turbidity SS (ppm)	DO (ppm)
Water supply conservation	6.5–8.5	≤25	≥7.5
Fisheries and recreation	6.5–8.5	≤50	≥5
Industrial/Agricultural and conservation of the environment	6.0–8.5	≤100 No observable floating matter	≥2
River Sabaki ^a	7.66	220 (FTU)	8.0 (95%)
River Ramisi ^a	7.36	19.0 (FTU)	6.4 (80%)
River Vevesi ^a	6.33	3.5	4.6 (58%)

^a Data obtained in this study. Other data from Ochieng (1987)

227 high indicating that the water at the sampling point would
228 not be suitable for direct drinking and industrial use as well
229 as for fish and other animal habitat.

230 The pH and DO values obtained for the three rivers were
231 within international standard requirements for water supply
232 for fisheries, recreation and industrial, agricultural and
233 environmental conservation (Ochieng et al. 2006). The
234 turbidity of the water from Sabaki was much higher (~10–
235 60 times) than those of the other two rivers in the study.
236 This river originates from Athi River which flows through
237 agricultural region in central Kenya and is bound to carry
238 more organic and sediment particles compared with the
239 others in the study and therefore siltation could have
240 occurred at the sampling points.

241 The concentrations of leachable heavy metals in sedi-
242 ment samples from three sampling sites are shown in
243 Table 3. Some metals such as Ag, Cd and Cr were poorly
244 extracted under the low acid strength employed or were
245 extracted at concentrations below the detection limits.
246 Generally most of the exchangeable cations in the estuarine
247 sediments ranged between 2% and 20% of the total trace
248 metal content obtained by digestion with concentrated acid.
249 Co, Cu, Mn, Ni and Zn were fairly exchangeable and
250 therefore represented the most mobile species in the

Table 3 Total leachable concentration (µg/g dry weight) of heavy metals in sediment samples from the three sites

Metal species	Ramisi (RMS2)	Vevesi (VVS)	Sabaki (SB)
Ag	Bdl	Bdl	Bdl
Cd	Bdl	Bdl	Bdl
Co	0.53	0.17	0.10
Cr	Bdl	Bdl	Bdl
Cu	1.17	0.39	0.78
Mn	506.75	380.06	29.24
Ni	6.82	3.90	3.90
Pb	Bdl	Bdl	1.56
Sn	23.39	Bdl	Bdl
Zn	Bdl	7.18	35.08

Bdl below the detection limit

sampling sites. Exchangeable cations seldom constitute the bulk of the total supply and often represent only a small fraction of total which supports the results obtained in this study.

Weak acids digest only leachable and particle bound metals but strong acids dissolve constitutive metals from the mineral matrix, in addition. Spatial distribution of heavy metals in surface sediments is as a result of integrated changes occurring in the water column and concentrations of heavy metals in the sediment represent combination of chemical, biological and physical processes occurring in fluvial, estuarine and coastal environment. Solid surface chemistry influences cation exchange reactions and therefore controls adsorption and the proportion of leachable cations. Manganese oxides, for example, have high surface areas and high cation exchange capacities and act as strong scavengers for heavy metals such as Cr. In this case in sediments with high Mn in the matrix one would expect lower leachable concentration of Cr. The total exchangeable cations of the sediments are the proportions of the cations associated with the sediment solids that are subject to interchange with cations in solutions and aquatic biota, under conditions of little or no decomposition of the remainder of the sediments. They are chemically the most reactive part of the sediments. Cations in solution remain nearly at equilibrium with those in exchangeable form.

It is known that a large percentage of heavy metals in non-polluted lakes and rivers are generally incorporated in the crystal lattice of minerals that make up the bottom mud. This percentage would form part of the natural background level in the bottom mud in polluted waters on which the anthropogenic input would be based on. However, the concentration factors would be expected to change from time to time depending on the mixing patterns of the water, the water chemistry as well as on accumulation that in turn depends on nutrients and organic matter in the water column. The heavy metals that are not present in the crystal lattice are therefore distributed in organic matter, in hydrous Mn and Fe oxides, and in any discrete minerals formed by the metals.

The mean total concentrations in sediment samples from the four sampling sites are shown in Table 4. The three

Table 4 Mean total trace metal concentration in sediment ($\mu\text{g/g}$ dry weight) compared with background and shale concentrations

River	Ag	Cd	Co	Cr	Cu
SB	0.27 ± 0.21	0.12 ± 0.21	0.39 ± 0.12	ND	5.55 ± 1.11
RMS1	18.52 ± 1.34	0.21 ± 0.13	0.96 ± 0.24	3.63 ± 0.24	23.47 ± 4.11
RMS2	0.27 ± 0.11	0.04 ± 0.05	0.24 ± 0.11	ND	1.46 ± 0.35
VVS	0.27 ± 0.22	0.39 ± 0.20	1.00 ± 0.33	2.92 ± 1.10	19.49 ± 4.44
Back ^a	NL	0.2 ± 0.1	6.4 ± 1.5	21.6 ± 6.9	21 ± 6.4
Shale ^b	NL	0.3	NL	NL	45

River	Mn	Ni	Pb	Sn	Zn
SB	97.45 ± 11.5	9.55 ± 1.55	6.24 ± 1.44	38.98 ± 7.56	277.4 ± 110.2
RMS1	917.37 ± 101.1	16.44 ± 4.2	26.21 ± 4.12	41.16 ± 10.2	83.61 ± 22.1
RMS2	204.65 ± 40.4	ND	4.09 ± 3.11	38.98 ± 11.0	6.33 ± 3.21
VVS	360.57 ± 56.2	25.34 ± 6.22	27.29 ± 3.33	56.52 ± 12.1	93.55 ± 15.4
Back ^a	479 ± 64	NL	23 ± 3.7	NL	56 ± 25
Shale ^b	NL	NL	20.0	NL	95.0

SB Sabaki, RMS1 Ramisi site 1, RMS2 Ramisi site 2, VVS Vevesi, ND not detected, NL not in literature cited

^a Background levels (Adamo et al. 2005)

^b Average Shale concentrations (Jain 2004), $n = 3$

292 rivers showed normal trend of trace metal contents in
 293 sediment except for elevated levels of Zn ($277.4 \mu\text{g/g}$ dry
 294 weight) in Sabaki River. Sediment samples taken ~ 1 km
 295 away downstream from Ramisi Sugar factory (i.e. at
 296 Ramisi Bridge) gave higher concentrations of metals than
 297 those sampled before the factory (i.e. at Daragube point),
 298 those taken even farther downstream from the factory at
 299 River Vevesi (a tributary of Ramisi) and those in Sabaki
 300 River. The factory effluents may either have contained
 301 traces of heavy metals that contributed to higher concen-
 302 trations observed or the effluent may have enhanced
 303 deposition of heavy metals onto bottom sediments if it
 304 contained high organic load.

305 The three coastal rivers had relatively lower mean sedi-
 306 ment total concentrations of heavy metals Cd, Cr, Cu and
 307 Pb than those reported in Dipsiz stream in Turkey and
 308 Naples Harbour in Italy (Adamo et al. 2005; Demirak et al.
 309 2006). The range of mean total sediment concentrations (in
 310 $\mu\text{g/g}$ dry weight) of Cd (from 0.04 to 0.39) was lower than
 311 those found in Yamuna River in India (mean of 9.5), Dipsiz
 312 stream in Turkey (0.80 ± 0.60) and Naples harbour in Italy
 313 (mean of 0.9; Jain 2004; Adamo et al. 2005; Demirak et al.
 314 2006) but was comparable with that of Keelung river in
 315 Taiwan (range 0.073–0.70; Huang and Lin 2003). This tells
 316 us that the rivers investigated in our study were less
 317 exposed to anthropogenic inputs compared with the Euro-
 318 pean waters. The level of Cd was also comparable to
 319 background levels as reported for Naples Harbour
 320 (0.2 ± 0.1) and shale concentrations (mean of 0.3; Jain
 321 2004; Adamo et al. 2005). The ranges of the mean sedi-
 322 ment concentrations of Co (0.24–1.0), Cr (ND–3.63) and

323 Cu (1.46–23.47) were also lower than those of Naples
 324 harbour (means 5.1, 72.5, and 131, respectively). The Cr
 325 and levels were also lower than those of Dipsiz stream
 326 (mean of 19.70) and the background levels reported in Italy
 327 (21.6 ± 6.9). The mean Cu sediment concentration level
 328 was comparable to those reported for Yamuna River (mean
 329 of 22.2) and Keelung river (range 12–110) and Dipsiz stream
 330 (13 ± 9.0), but comparable to background (21.0 ± 2.5).
 331 Mean total Pb sediment concentration levels (range 4.09–
 332 27.27) also showed lower values compared with Naples
 333 harbour (mean 131), Yamuna river (mean of 60.3) and
 334 Dipsiz stream (83.60 ± 56.2) but the mean range for Zn
 335 (range 6.33–277.4) was comparable with Yamuna river
 336 (mean 59.2), Keelung (range 57–270), Dipsiz stream
 337 (37.00 ± 26.0) and Naples harbour (mean of 303). The
 338 values obtained for Mn were comparable with those of
 339 Keelung river (range 330–600) and Naples harbour (mean
 340 389). All these show more anthropogenic influence con-
 341 tributing to higher concentrations of Co, Cd, Cu, Pb and Zn
 342 in some the European and Asian ecosystems. Ramisi
 343 sampling point after the former Ramisi Sugar Factory had
 344 higher levels of metals than Sabaki and Vevesi. This was
 345 mainly due to influence of the sugar factory. Sabaki River
 346 concentrations could be considered to be due to its geo-
 347 logical origin as well as industrial effluent upstream such as
 348 the factories in Athi River and tannery factory in Thika.
 349 But in general all these three rivers would be considered
 350 non-polluted in terms of sediment loads, based on shale
 351 standard and the background concentrations. A comparison
 352 of metal concentration in sediment with shale standard is
 353 generally taken as a quick practical method of tracing

354 heavy metal enrichment (Wedepohl 1995; Jain 2004;
355 Warren et al. 2005).

356 Everaarts and Nieuwenhuize (1995) obtained lower
357 concentrations (in $\mu\text{g/g}$ dry weight) of Cu (0.100), Zn
358 (0.524), Cd (0.0117), Pb (0.137) and Mn (1.587) in estu-
359arine sediment samples taken from Sabaki River mouth at
360 the Indian Ocean Coast of Kenya (Everaarts and Nie-
361 uwenhuize 1995). This is expected because of mixing of
362 the river water and the Indian Ocean water at the estuaries
363 as his sampling points were more inside the ocean. In Lake
364 Kariba in Zimbabwe the reported mean surface sediment
365 concentrations (in $\mu\text{g/kg}$) were comparable with R. Sabaki
366 and ranged within 15.8–25.8 (Cr), 0.69–0.72 (Cd), 12.4–
367 16.1 (Cu), 19.3–23.9 (Pb), 238.7–326.9 (Mn), 23.2–5.9
368 (Ni) and 68.2–71.1 $\mu\text{g/kg}$ (Zn), in Kasse bay and in
369 Cages (Berg et al. 1995). In the drainage basin of Lake
370 Kariba metal (Cu, Mn, Pb and Zn) mining takes place and
371 elevated levels above natural concentrations in the eco-
372 system are attributed mainly to these mining activities.

373 The dissolved metal concentrations of waters samples
374 taken from the four sampling sites are presented in Table 5.
375 The concentration levels of most of the heavy metals
376 analysed are within acceptable range and, the waters would
377 considered suitable for drinking and for aquatic life forms
378 such as fish (see Table 6). The concentration levels also
379 pass the World Health standards for drinking water and the
380 USEPA maximum concentration but do not conform to
381 USEPA criteria of continuous concentration. However, the
382 concentrations of Ag, Ni, Pb and Mn were above accept-
383 able levels and more analysis should be done to confirm
384 these high concentrations and to ascertain their sources. In
385 Table 6, the concentrations of toxic metals in waters of
386 rivers in Turkey, Italy and South Africa are included for
387 comparison.

388 One method of showing metal enrichment in sediment is
389 by comparison of metal concentration ratios, where species
390 concentrations are expressed as ratios of conservative

391 metals which occur in much higher concentrations such as
392 Al, Mn and Fe (Jain 2004). The ratios of trace elements can
393 reveal geochemical imbalances shown in elevated trace
394 levels, where high metal concentration ratios (e.g. M/Mn)
395 are normally attributed to anthropogenic activities. The
396 metal/Mn ratios for dissolved metal species ranged from
397 6.56×10^{-3} (Cd) to 2.205×10^{-1} (Zn) in River Sabaki
398 water, from 3.448×10^{-2} (Ag) to 2.86 (Sn) in River
399 Ramisi site 1, and from 2.17×10^{-3} (Ni) to 6.5×10^{-1}
400 (Zn) in River Ramisi site 2. No concentrations of Mn were
401 determined in Vevesi water consequently no values of
402 metal/Mn ratios for this river were calculated. The metal/
403 Mn ratios for sediments ranged from 1.23×10^{-3} (Cd) to
404 2.846 (Zn) in Sabaki, 2.29×10^{-4} (Cd)– 9.11×10^{-2} (Zn)
405 for Ramisi 1, 1.95×10^{-4} (Cd)– 1.90×10^{-1} (Sn) for
406 Ramisi 2 and from 7.48×10^{-4} (Ag) to 2.59×10^{-1} (Zn)
407 in Vevesi. For dissolved metals, the data indicate higher
408 concentration/enrichment of Ag in Sabaki River, Cd in
409 Ramisi and Ni in Sabaki and Pb in Ramisi, respectively
410 attributable to recent discharge from factory effluent. In
411 sediments, the metal/Mn ratios showed higher concentra-
412 tion/enrichment of Ag in Ramisi, Cd in Sabaki and Vevesi,
413 and Zn in Sabaki. Some of these metal/Mn ratios can be
414 supported by EF (Enrichment Factor) values in Table 7
415 showing enrichment of Cd, Pb and Zn in R. Sabaki and R.
416 Vevesi. The high EF indicate contamination in Sabaki
417 River as it flows through Thika and Athi River industrial
418 regions and contamination of River Vevesi by the former
419 Ramisi Sugar factory. The metal/Mn ratios show discharge
420 from Factory effluent at Ramisi River in the water at site 2,
421 and the sediment EF ratios also confirm enrichment of Cd
422 and Pb in both sites in Ramisi.

423 In conclusion, the sampling points considered in this
424 study provided a suitable indication of anthropogenic
425 inputs and sediment enrichment of toxic heavy metals
426 including Cd, Pb, and Zn in Rivers Sabaki, Vevesi and
427 Ramisi which discharge in to the Indian Ocean coast of

Table 5 Dissolved metal concentration in river water ($\mu\text{g/L}$)

River	Ag	Cd	Co	Cr	Cu
SB	100 ± 12.4	5.0 ± 2.22	36 ± 4.12	25 ± 2.44	22.5 ± 6.22
RMS1	4.0 ± 2.11	5.0 ± 1.68	6.0 ± 2.30	7.6 ± 1.34	10 ± 2.10
RMS2	3.0 ± 1.44	8.0 ± 2.11	6.0 ± 3.10	4.3 ± 2.10	45 ± 10.4
VVS	ND	ND	ND	25 ± 5.40	7.5 ± 2.22
River	Mn	Ni	Pb	Sn	Zn
SB	762 ± 101.2	81 ± 6.21	68 ± 4.40	ND	168 ± 46.2
RMS1	116 ± 12.54	13 ± 2.11	7.0 ± 2.30	300 ± 16.4	75.5 ± 13.6
RMS2	138 ± 13.40	0.3 ± 0.02	34 ± 5.44	ND	91 ± 15.7
VVS	ND	13 ± 3.12	25 ± 3.40	ND	33 ± 10.4

Note: SB Sabaki, RMS1 Ramisi site 1, RMS2 Ramisi site 2, VVS Vevesi, ND not detected, n = 3

Table 6 Mean concentrations (in µg/L) of some toxic metals determined in the three coastal river waters compared with those of WHO (1998) and USEPA (1999) acceptable standard limits, background and other levels determined in other rivers

Limit	Ag	Cd	Cr	Cu	Mn	Ni	Pb	Zn
HDL ^a	NL	NL	NL	50	50	NL	NL	5 × 10 ³
MPL ^a	50	10	50	1 × 10 ³	500	NL	100	1.5 × 10 ⁴
USEPA CMC ^b	NL	4.3	16	13	NL	NL	65	120
USEPA CCC ^b	NL	2.2	11	9	NL	NL	2.5	120
TC ^c	10	10	50	2 × 10 ⁴	NL	50	100	100
Sabaki ^d	100	5.0	25	22.5	762	81	68	168
Ramisi 1 ^d	4.0	5.0	7.6	10	116	13	7.0	76
Ramisi 2 ^d	3.0	8.0	4.3	45	138	0.3	34	91
Vevesi ^d	ND	ND	2.5	7.5	ND	13	25	33
Gediz ^e	NL	2–8	1–17	4–84	NL	NL	10–110	3–46
Lambro ^f	NL	0.1–4.8	2–66	1.1–134	NL	NL	2.2–139	NL
Dipsiz ^g	NL	0.17	0.09	0.37	NL	NL	0.41	1.05
Dzindi ^h	NL	1.6–3.3	NL	2.1–2.6	NL	NL	10.5–12.3	2.1
Back ⁱ	NL	0.02	NL	1.00	NL	NL	0.20	10

NL not in literature cited, ND not determined, HDL highest desirable level in drinking water, MPL maximum permissible level in drinking water

^a WHO (1981)

^b CMC criteria maximum concentration, CCC criteria continuous concentration

^c TC threshold concentration for aquatic life (fishes) tolerance

^d Levels obtained in this study

^e Gediz river

^f Lambro River in Italy (Adamo et al. 2005)

^g Dipsiz stream in Turkey

^h Background concentration (Demirak et al. 2006)

ⁱ Dzindi River in S.Africa (Okonkwo et al. 2005)

428 Kenya which can influence their deposition and accumu- 439
429 lation in the coastal environment. These enrichments were 440
430 influenced by inputs upstream from the central regions of 441
431 Kenya and by the Ramisi Sugar factory effluent. The total 442
432 exchangeable sediment cations results showed that Cu, Mn, 443
433 Ni, Pb and Zn were fairly exchangeable and their leach- 444
434 ability could have been influenced by organic carbon loads, 445
435 recent anthropogenic discharge and redox conditions in the 446
436 rivers. In general, exchangeable cations in sediment ranged 447
437 from 0.10 to 506.75 µg/g for Co, Cu, Mn, Ni, Pb, Sn and 448
438 Zn constituting between 2% and 20% of total metal 449

concentrations obtained by digestion with strong acid. The 439
leachable Cu, Mn, Ni, Pb and Zn therefore represent the 440
most mobile species in the sampling sites. For dissolved 441
metals, the metal/Mn ratios indicate higher concentrations 442
of Ag in Sabaki River, Cd in Ramisi, Ni in Sabaki and Pb 443
in Ramisi, respectively. In sediments, the metal/Mn ratios 444
show higher enrichment of Ag in Ramisi, Cd in Sabaki and 445
Vevesi, and Zn in Sabaki, respectively. Enrichment factors 446
(EF) also confirm elevated levels of Cd, Pb and Zn in 447
sediment in River Sabaki and River Vevesi which were due 448
to anthropogenic inputs through Athi River. The mean total 449

Table 7 Enrichment factors (EF) based on Mn and given mean crust concentrations

Metal species	Mean crust concentration (µg/g) ^a	Sabaki	Ramisi 1	Ramisi 2	Vevesi
Mn	950				
Cd	0.11	7.798	1.977	1.688	9.340
Cu	50	1.082	0.486	0.136	1.027
Pb	14	4.345	1.938	1.356	5.136
Zn	75	36.057	1.161	0.392	3.286

^a Huang and Lin (2003), EF = (X/Mn)_{sample}/X/Mn_{crust}, where X concentration of metal species, Mn concentration of Mn

450 dissolved metal concentration ranges for the three rivers
451 were comparable with those ranges reported in rivers in
452 South Africa (Okonkwo et al. 2005) but the sediment
453 concentrations were below those of rivers in Europe and
454 Asia where anthropogenic addition of some of the toxic
455 elements such as Cu, Pb and Cd is evidently higher.

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